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Heterogeneous photo-Fenton oxidation of methylene blue solution using Fe(II)-montmorillonite calcinated clay catalyst

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Session L. Student Session

1 – 15 December 2022

Introduction

Contributes to fulfilling the basic living (clothing) requirements of human life;

The wastewater discharged from textile dyeing industry contains a total of 72 toxic chemicals, out of which 30 chemicals cannot be removed by waste treatment processes;

Formation of many types of cancers of different organs such as bladder, spleen, liver and normal aberrations in model organisms and chromosomal deformities in mammalian cells;

Textile dyes are characterized by high color density, high concentration of recalcitrant organics and pH and high turbidity.



Textile dye factory



River polluted by textile dyes



Textiles wastewater treatment technology: A review

Dongyang Deng,^{1,*} Mehdi Lamssali,¹ Niroj Aryal,² Andrea Ofori-Boadu,¹ Manoj K. Jha,³ Raymond E. Samuel⁴

CRITICAL REVIEWS IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY
2017, VOL. 47, NO. 19, 1836–1876
<https://doi.org/10.1080/10643389.2017.1393263>



Biological methods for textile dye removal from wastewater: A review

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Review article

Textile finishing dyes and their impact on aquatic environs

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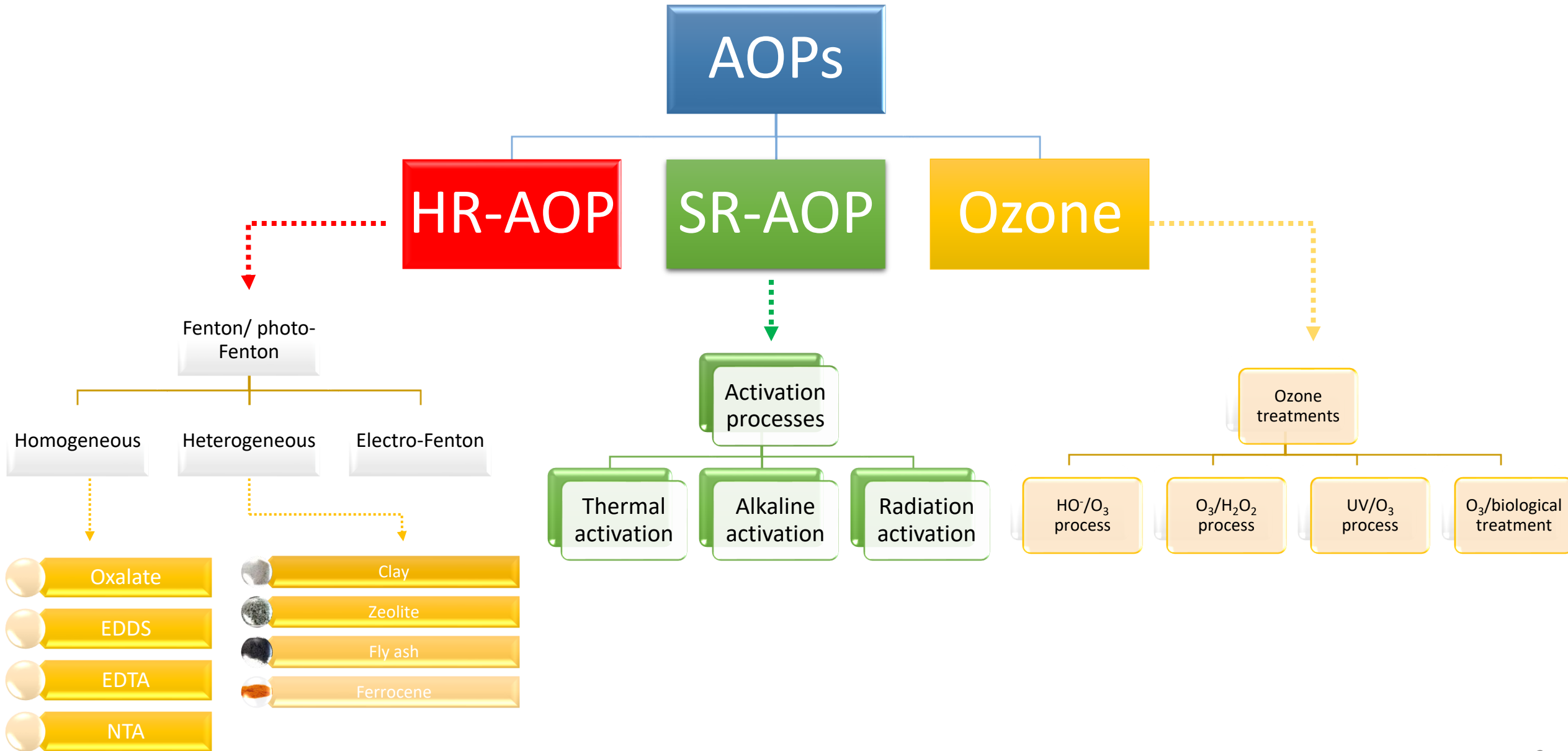
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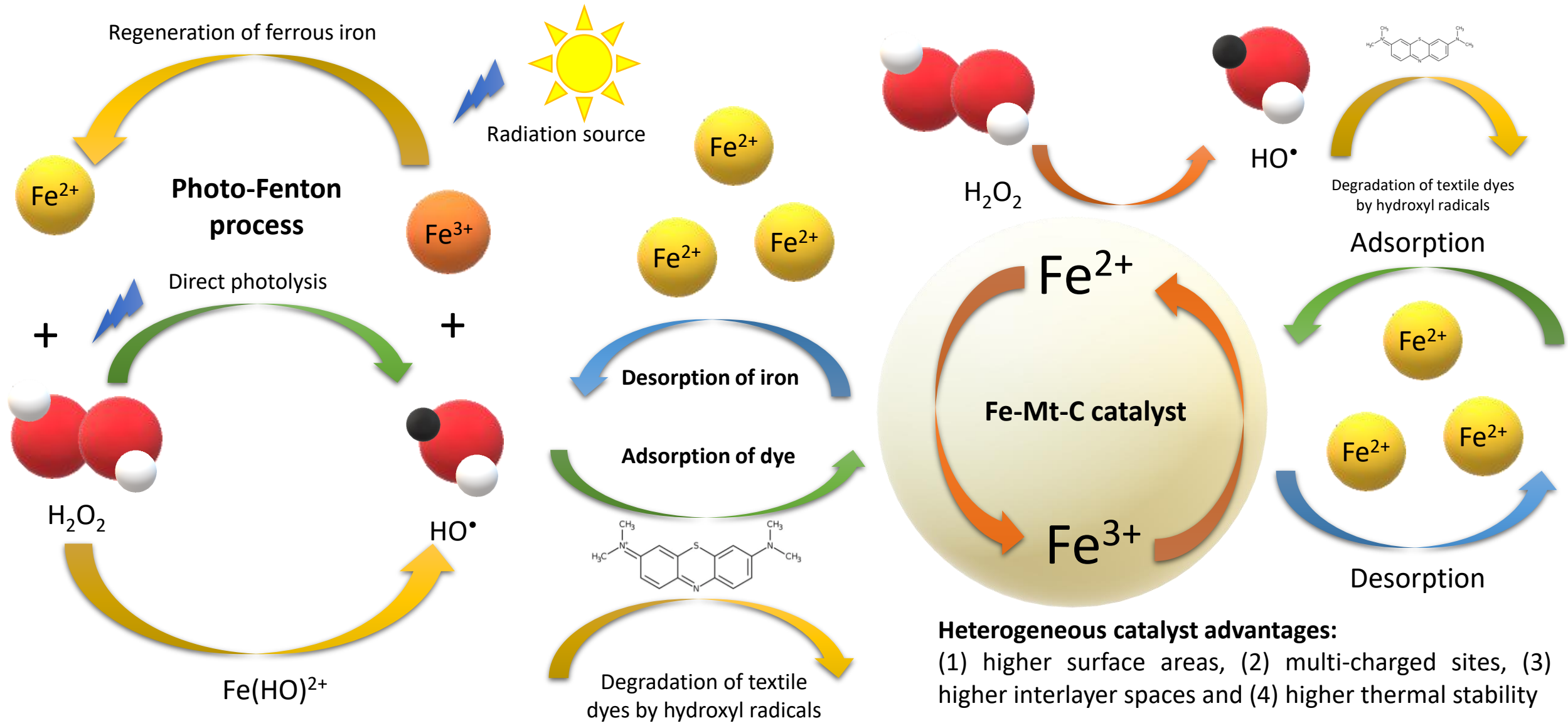
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Mechanism of the heterogeneous photo-Fenton process

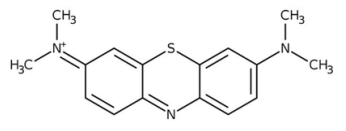


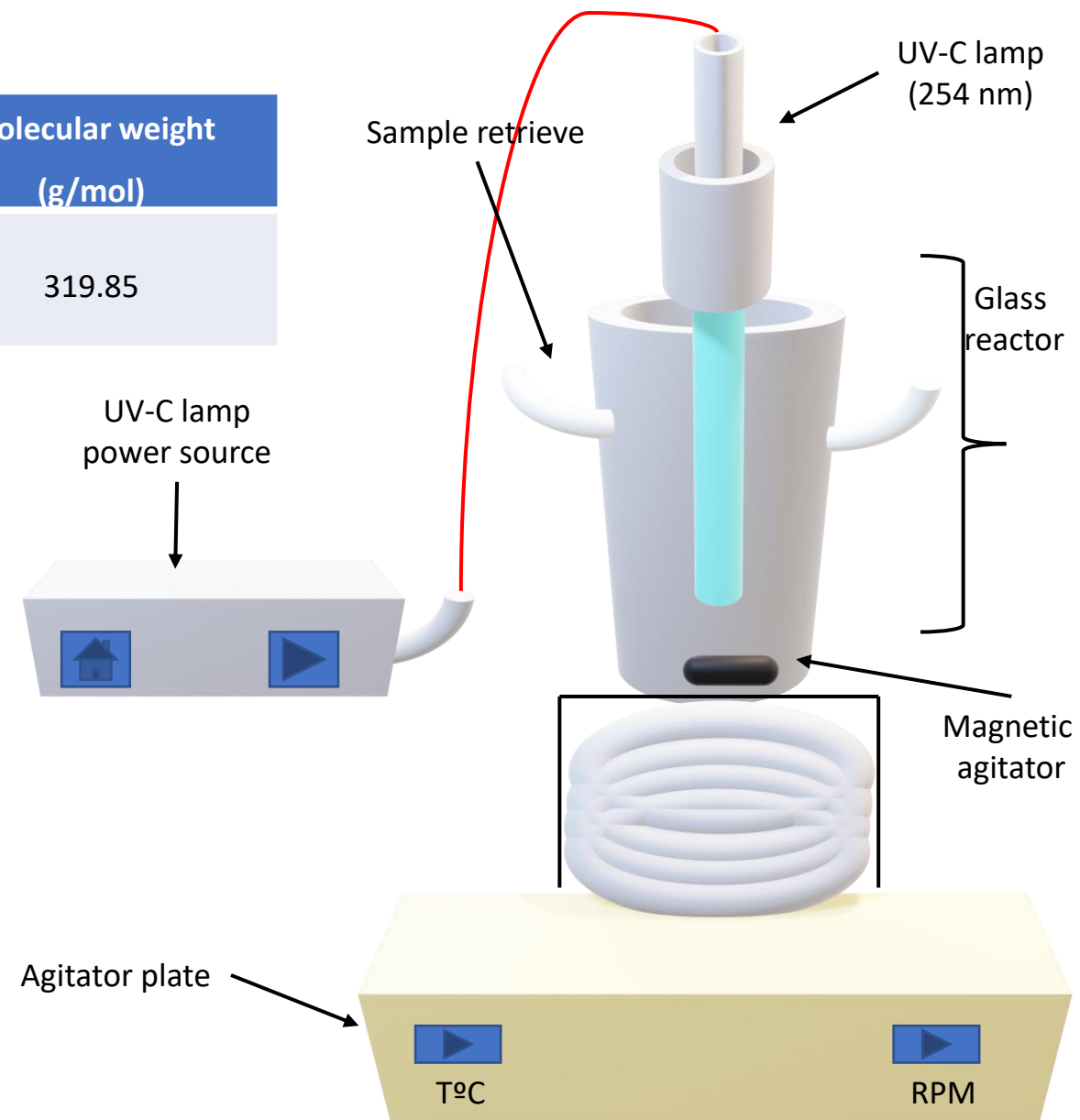
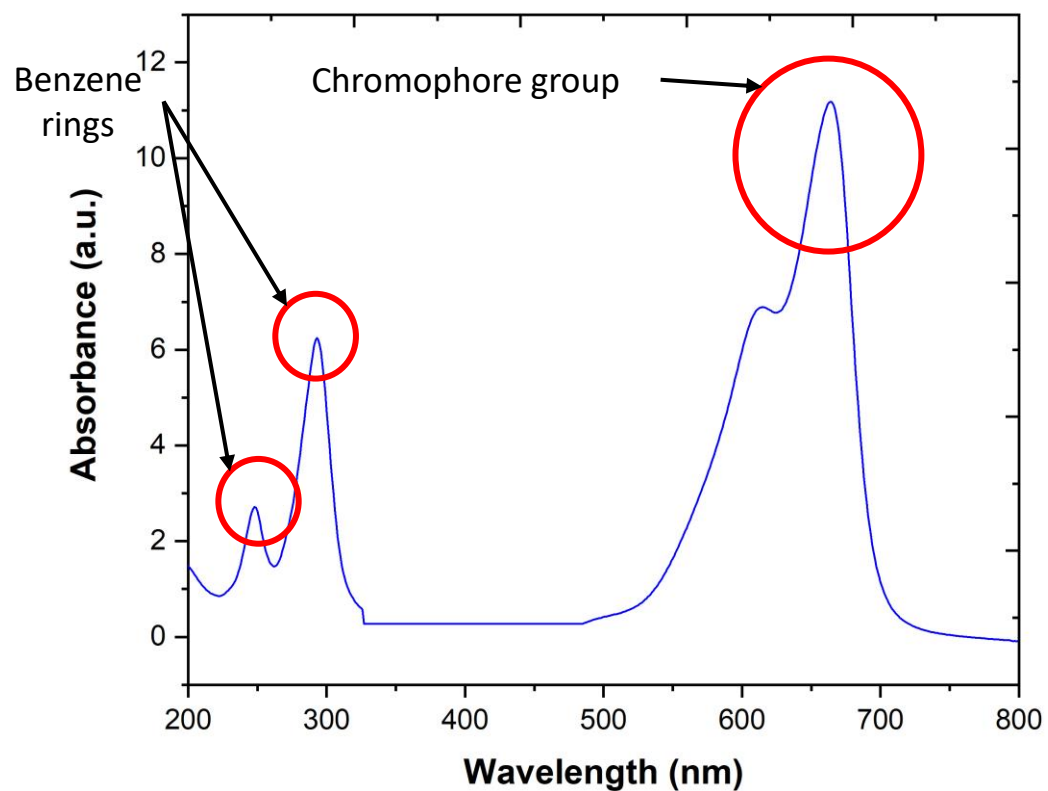
Heterogeneous catalyst advantages:
 (1) higher surface areas, (2) multi-charged sites, (3) higher interlayer spaces and (4) higher thermal stability

The aim and novelty of this work is:

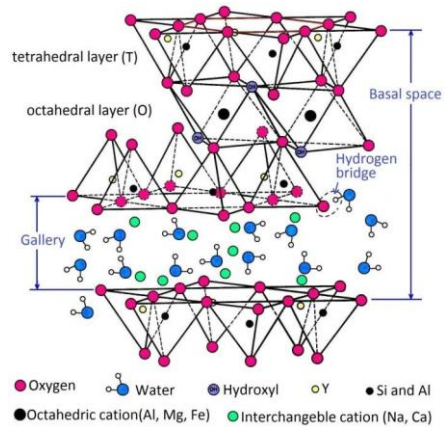


(1) to develop a new catalyst using a montmorillonite clay as a base material, to degrade a textile dye

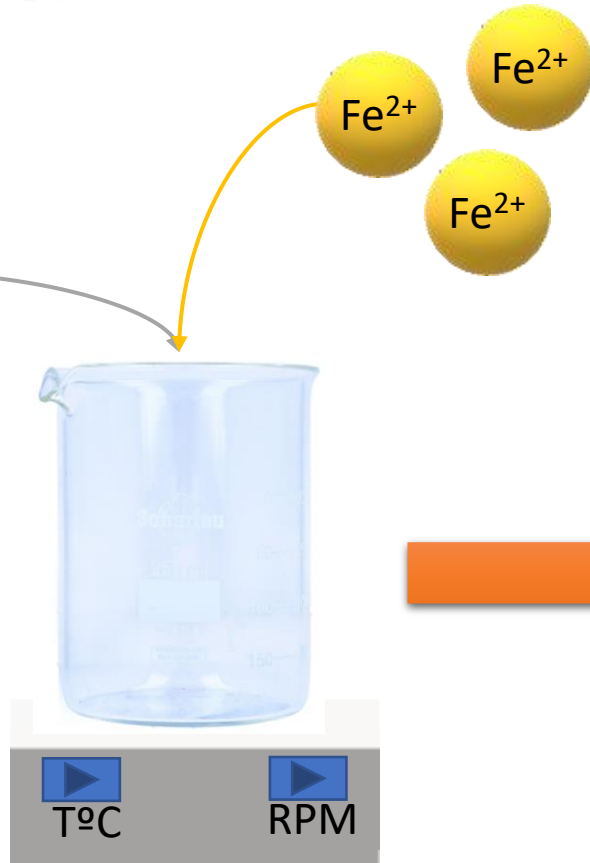
Name	Chemical structure	λ_{\max} (nm)	Molecular weight (g/mol)
Methylene blue (azo dye)		665, 300 and 250 nm	319.85



Catalyst preparation



Activated sodium bentonite (Na-Mt)



Na-Mt



Fe(II)-Mt



Incubator



- Calcination (500°C/ 4 h)

- Drying for 24 h at 70°C

- Agitation at 300 RPM/ 100°C;
- Agitate until all water is evaporated

Characterization of Fe-BC catalyst

- The FTIR analysis (Figure 1(a)) showed similar peaks between the Na-Mt and Fe(II)-Mt. However, the Fe(II)-Mt revealed a significant structural change, with the disappearance of a peak at 1103.28 cm^{-1} and the appearance of a new peak at 528.49 cm^{-1} .
- The XRD patterns of both Na-Mt and catalyst Fe(II)-Mt are shown in Figure 1(b), and the crystallographic parameters were evaluated by measuring the basal reflexions in the plane dhkl 001. The data revealed a significant shift associated with the reflection d001, from 14.01 \AA to 9.92 \AA , confirming the structural modifications that occurred on the Fe(II)-Mt after the calcination.

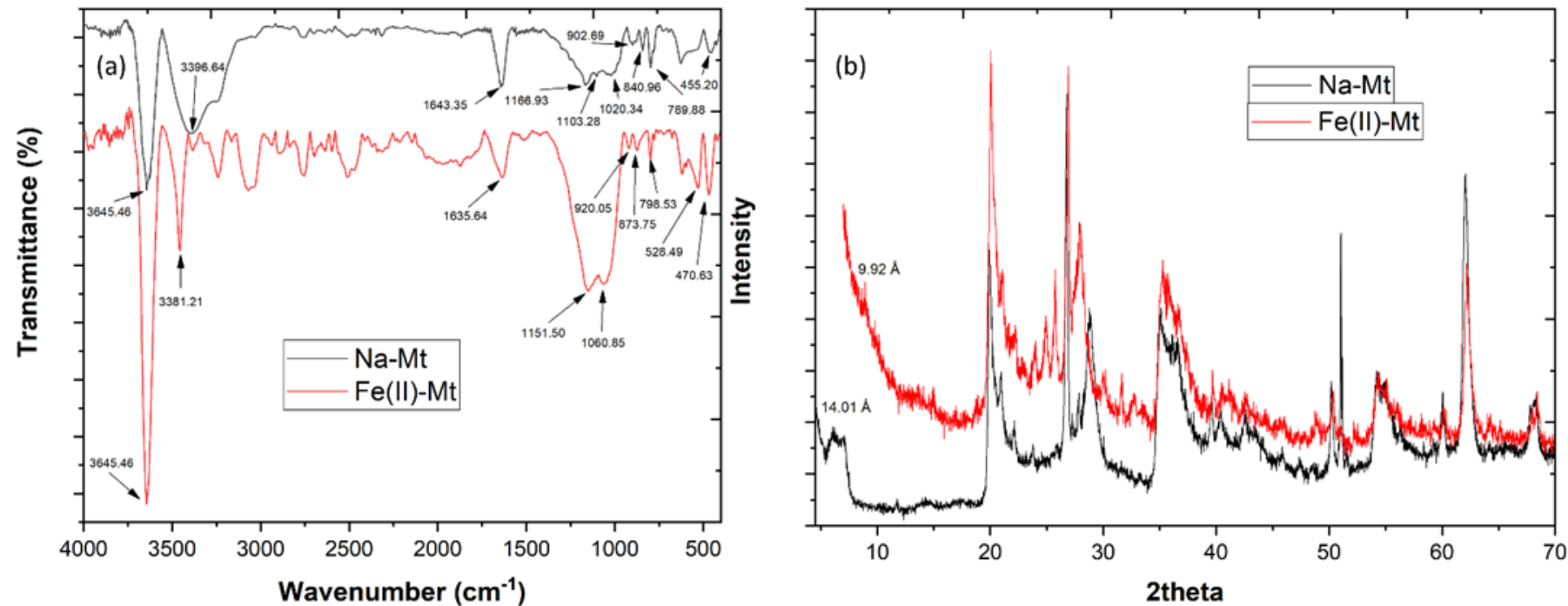
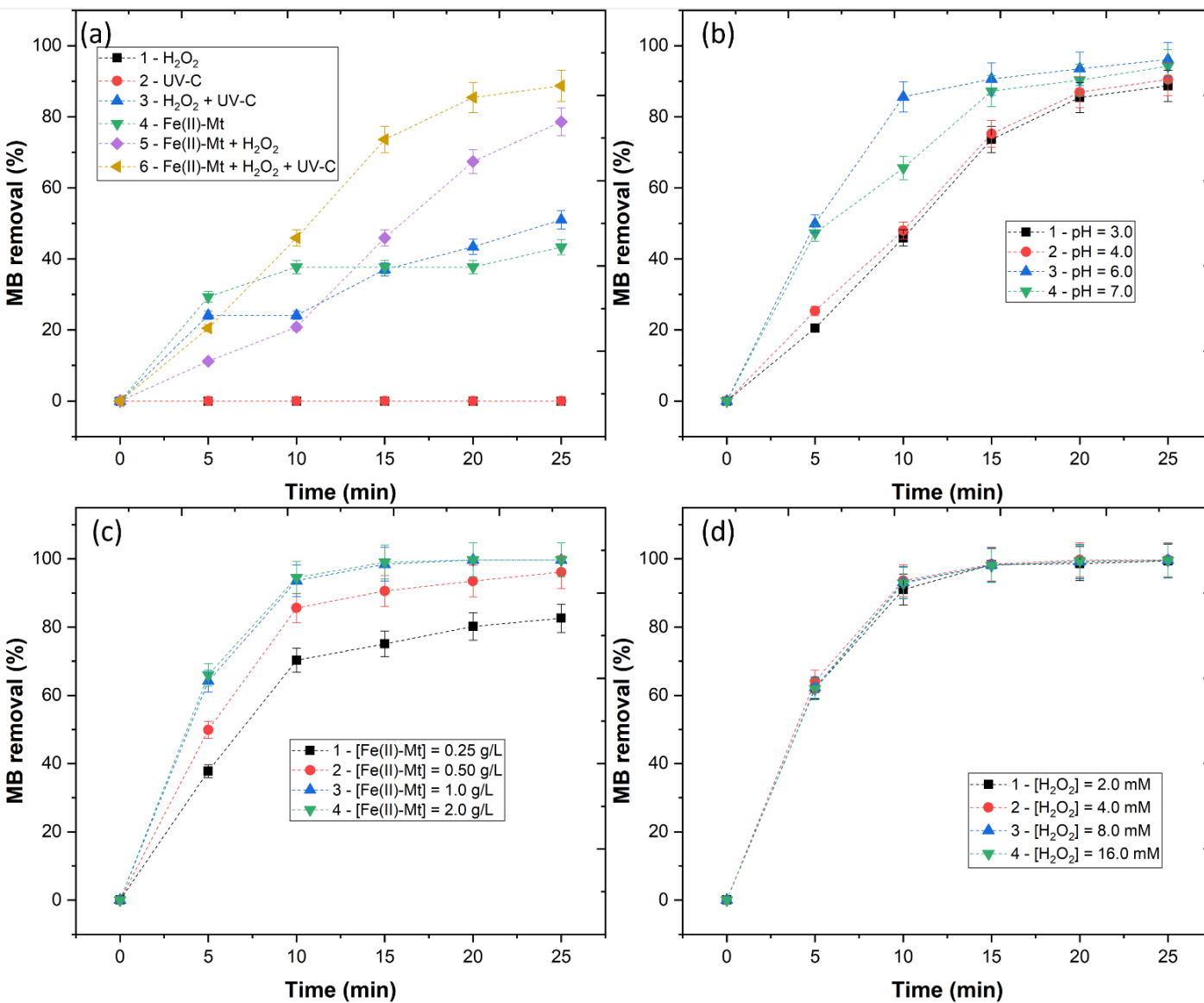


Figure 1. Analysis of Na-Mt and Fe(II)-Mt by (a) FTIR and (b) X-ray diffraction.

Results and discussion



- In Figure 2(a), six different AOPs were tested, with the following conditions: pH = 3.0, [Fe(II)-Mt 0.5M] = 0.5 g/L, [H₂O₂] = 4 mM, [MB] = 0.16 mM, radiation = UV-C (254 nm), time = 25 min;
- heterogeneous Fenton and photo-Fenton were applied, with results showing a MB removal of 78.6 and 88.7%. Clearly, the catalyst can convert the H₂O₂ and generate HO• radicals. This effect is enhanced with the application of UV radiation, thus heterogeneous photo-Fenton was selected as the best AOP;
- The pH was varied from 3.0 to 7.0 (Figure 2(b)). Results showed a MB removal of 88.7, 90.5, 96.1 and 94.2%, respectively for pH 3.0, 4.0, 6.0 and 7.0;
- The results in Figure 2(c) showed a MB removal of 82.6, 96.1, 99.7 and 99.7%, respectively for 0.25, 0.50, 1.0 and 2.0 g/L. As the catalyst concentration increased from 0.25 to 1.0 g/L, the production of HO• radicals increased, due to a higher content of Fe²⁺ present in solution;
- The H₂O₂ concentration was varied from 2.0 to 16.0 mM to access the effect of the oxidant concentration in heterogeneous photo-Fenton (Figure 2(d)). The results showed that the removal of MB was independent from the concentration of H₂O₂.

Figure 2. Removal of MB by (a) variation of AOPs, (b) variation of pH (3.0 – 7.0), (c) variation of Fe(II)-Mt catalyst concentration (0.25 2.0 g/L) and (d) variation of H₂O₂ concentration (2.0 – 16.0 mM).

Catalyst reuse

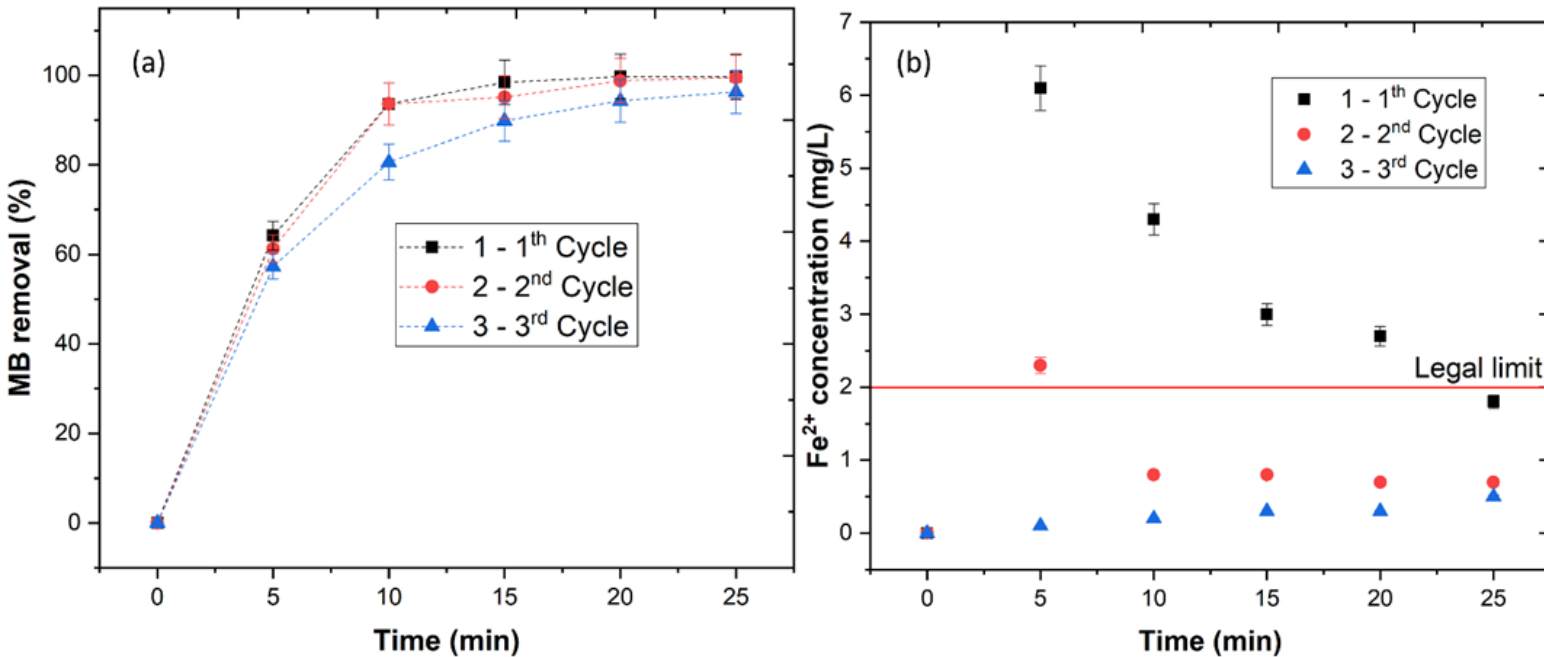


Figure 3. (a) Catalyst stability, (b) Fe²⁺ leaching concentration for 3 consecutive cycles.

- 3 consecutive cycles were performed. The results in Figure 3(a) shows a MB removal of 99.7, 99.5 and 96.3%, respectively for the 1st, 2nd and 3rd cycles;
- The leaching concentration was determined during the 3 cycles (Figure 3(b)). These results showed a high Fe²⁺ release during the first 5 min, decreasing its concentration from 5 to 25 min;
- The final Fe²⁺ concentration values were observed to be far below the European Eco-nomic Community standards for discharge of treated waters – 2 mg L⁻¹.

Conclusions

Based in the results, it is concluded:



(1) that calcination of montmorillonite clays does not affect their structural integrity and allows the incorporation of Fe^{2+}



(2) that the heterogeneous photo-Fenton is the most efficient process in MB degradation



(3) that the catalyst can be reused for 3 consecutive cycles, decreasing the treatment costs and the iron is reabsorbed after each cycle

Acknowledgements

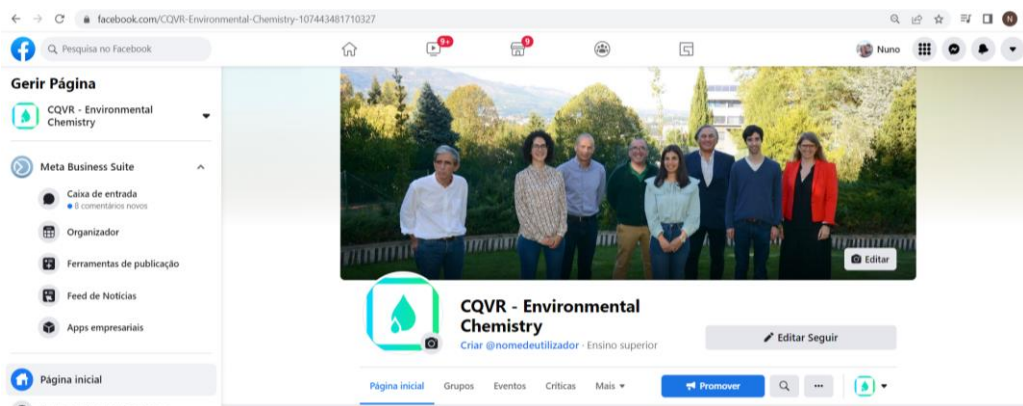
The authors are grateful for the financial support of the **Project AgriFood XXI**, operation nº NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to **CQVR** through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.



Thank you for your attention

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A aluna de Doutoramento Rita Teixeira, com a apresentação intitulada " Wastewater treatment for a responsible discharge" apresentou produtos inovadores à base de subprodutos gerados na agricultura e como podem ser reaproveitados para o tratamento de efluentes.

On the 8th of July, the Vila Real Chemistry Center celebrated its 20th anniversary. The Environmental Chemistry group had the opportunity to present their work. The PhD student Nuno Jorge, with a presentation entitled "Treatment of agro-industrial wastewaters by physico-chemical and advanced oxidation processes", showed some of the reactors developed in his thesis, as well as some of the products developed through plants. The PhD student Rita Teixeira, with a presentation entitled "Wastewater treatment for a responsible discharge" presented innovative products based on by-products generated in agriculture and how they can be reused for the treatment of effluents.



View Congress participations

Podem consultar o trabalho no site:
<https://sciforum.net/event/IEChO2022#awards>

The Environmental chemistry group congratulates the PhD student **Nuno Jorge** for the Best Paper award, entitled "Plants as natural organic coagulant powders for winery wastewater treatment".

The work can be consulted on the link:
<https://sciforum.net/event/IEChO2022#awards>



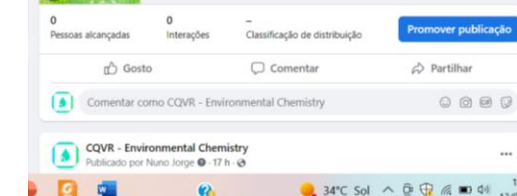
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In a few days (20 to 22 July) the Congress "5th International Conference on Green Chemistry and Sustainable Engineering (GreenChem-22)" will begin in Rome. The Congress has as Chairman Professor José Alcides Peres, belonging to the Environmental Chemistry group of the CQVR.
https://greenchem-europe.eu/_/JAPeres-short-CV-january...

The 5th International Conference on Green Chemistry and Sustainable Engineering (GreenChem-22) is organized by academics and researchers from different scientific areas from the University of Trás-os-Montes and Alto Douro, University of Salamanca, University of Santiago de Compostela, University of Extremadura, Hunan Agricultural University of China, Gogte Institute of Technology, University of Casimo and Southern Lazio, Universidad Complutense of Madrid and University of Las Palmas de Gran Canaria with technical support from Sciknowledge European Conferences.
The Congress program can be consulted on the website
<https://greenchem-europe.eu/>



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